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# Synthesis, spectroscopic characterization and biological activity on newly synthesized copper(II) and nickel(II) complexes incorporating bidentate oxygen–nitrogen hydrazone ligands

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#### ABSTRACT

We report the synthesis of the hydrazone ligands, 1-(phenyl-hydrazono)-propan-2-one (PHP), 1-(*p*-tolyl-hydrazono)-propan-2-one (THP), 1-[(4-chloro-hydrazono)]-propan-2-one (CHP), and their Ni(II) and Cu(II) metal complexes. The structure of the ligands and their complexes were investigated using elemental analysis, magnetic susceptibility, molar conductance and spectral (IR, UV, and EPR) measurements. IR spectra indicate that the free ligands exist in the hydrazo-ketone rather than azo-enol form in the solid state. Also, the hydrazo-NH exists as hydrogen bonded to the keto-oxygen either as intra or as intermolecular hydrogen bonding. In all the studied complexes, all ligands behave as a neutral bidentate ligands with coordination involving the hydrazone-nitrogen and the keto-oxygen atoms. The magnetic and spectral data indicate a square planar geometry for Cu<sup>2+</sup> complexes and an octahedral geometry for Ni<sup>2+</sup> complexes. The ligands and their metal chelates have been screened for their antimicrobial activities using the disc diffusion method against the selected bacteria and fungi. They were found to be more active against Gram-positive than Gram-negative bacteria. It may be concluded that the antimicrobial activity of the compounds is related to cell wall structure of bacteria.

Protonation constant of (PHP) ligand and stability constants of its  $Cu^{2+}$  and  $Ni^{2+}$  complexes were determined by potentiometric titration method in aqueous solution at ionic strength of 0.1 M sodium nitrate. It has been observed that the hydrazone ligand (PHP) titrated here has one protonation constant. The divalent metal ions  $Cu^{2+}$  and  $Ni^{2+}$  form with (PHP) 1:1 and 1:2 complexes. The insolubility of (THP) and (CHP) ligands in aqueous medium does not permit the determination of their protonation constants and formation constants of the corresponding complexes in aqueous solution.

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#### 1. Introduction

The preparation of a new ligand was perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligands, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [1,2]. Hydrazones were important class of ligands, such ligands have interesting ligation properties due to presence of several coordination sites [3]. Hydrazone ligands create an environment similar to biological systems by usually making coordination through oxygen and nitrogen atoms. Hydrazones were widely applied in the field of insecticides, medicines and analytical reagents for their excellent bioactivity properties [4]. Coordination chemistry of metal complexes of hydrazones [5] has gained a special attraction due to their biological activity and their ability to act as potential inhibitors for many enzymes [6,7]. Hydrazone derivatives possessing anti-inflammatory, analgesic [8–10], antipyretic [11], antibacterial [12] and antitumor [13] activities are also reported in the literature. In view of the above facts and the interest in studying the ligating behavior of such compounds [14–16], it is necessary to synthesize and characterize Cu<sup>2+</sup> and Ni<sup>2+</sup> solid complexes of the newly coordinating ligands, Scheme 1. The study also includes biological activity of the synthesized complexes.

## 2. Experimental

#### 2.1. Materials and reagents

CuCl<sub>2</sub>·2H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, HCl and KOH were provided by BDH. Aniline, P-chloro aniline, P-methyl aniline, ethyl acetoacetate and sodium nitrite were obtained from Sigma Chem. Company.





Abbreviations: PHP, 1-(phenyl-hydrazono)-propan-2-one; THP, 1-(p-tolylhydrazono)-propan-2-one; CHP, 1-[(4-chloro-hydrazono)]-propan-2-one. *E-mail address*: aelsherif72@yahoo.com

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**Scheme 1.** X = H (PHP); CH<sub>3</sub> (THP); Cl(CHP).

#### 2.2. Synthesis

#### 2.2.1. Synthesis of ligands

The ligands were synthesized according to the method reported in the literature [17] as follows: in a 4-l beaker equipped with a mechanical stirrer, 65 g (64 ml, 0.5 mole) of ethyl acetoacetate was added to 35 g (0.53 mole) of 85% potassium hydroxide in 1120 ml of water. The mixture is allowed to stand at room temperature for 24 h.

Forty-seven grams (48 ml, 0.5 mole) of aniline is dissolved in 200 ml of aqueous HCl (prepared from equal volumes of concentrated acid and water) in a 2-l beaker. The beaker is equipped with a mechanical stirrer and immersed in an ice-salt bath. After the solution has cooled to 0-5 °C, 36 g. (0.52 mole) of sodium nitrite dissolved in 1 liter of water is added slowly, with stirring, from a separatory funnel. The tip of the stem of the seperatory funnel dipped well below the surface of the liquid. The rate of addition is adjusted to maintain the temperature between 0 and 5 °C. A drop of the reaction mixture is tested from time to time with starch-io-dide paper until nitrous acid persists in the solution during a 5-min interval.

The solution of potassium acetoacetate is cooled to 0 °C, and 45 ml of concentrated HCl in 150 ml of ice water is added slowly with stirring. The diazonium salt solution is then added over a period of 20 min, and the mixture is made basic by the addition of 82 g of sodium acetate dissolved in 300 ml of water. The temperature of the reaction mixture is raised slowly to 50 °C and maintained at this temperature for 2 h; the separated solid is collected on a filter and dried. The yield of crude product is 72–77 g (89–95%). Purification can be effected by recrystallization from 200 ml of toluene. The purified product weighs 59–66 g (82%); m.p. 148–150 °C. The same method was applied for the preparation of THP and CHP except, P-methyl aniline and P-chloro aniline were used instead of aniline. Chemical equations for preparations are shown in Scheme 2.

#### 2.2.2. Synthesis of metal complexes

For the preparation of Cu(II) and Ni(II) complexes, the appropriate quantity of the hydrazone ligand (2 mmol) was dissolved in absolute EtOH (30 ml). To this solution an ethanolic solution of (1 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O or NiCl<sub>2</sub>·6H<sub>2</sub>O was added dropwise [1:2 molar ratio, M:L]. The resultant solution was refluxed for 4–5 h at 90 °C. The precipitated complexes were then filtered off, washed with petroleum ether and dried overnight in a vacuum desiccator. Elemental analysis data and yield are given in Table 1.

#### 2.3. Antimicrobial activity

The hydrazone ligands and their metal complexes were evaluated for their antibacterial activity against *Staphylococcus aureus* 

$$CH_3COCH_2CO_2C_2H_5 + KOH \rightarrow CH_3COCH_2CO_2K + C_2H_5OH$$

 $CH_3COCH_2CO_2K + HCl \rightarrow CH_3COCH_2CO_2H + KCl$ 

$$CH_{3}COCH_{2}CO_{2}H + P-C_{6}H_{5}N=NCl \rightarrow P-C_{6}H_{5}NH-N=CHCOCH_{3}+CO_{2}+HCl$$

(as Gram-positive bacteria) and *Pseudomonas aereuguinosa* and *Escherichia coli* (as Gram-negative bacteria) and also for their antifungal activity against *Candida albican* and *Candida lypolytica* using the disc diffusion method [18]. Moreover, some of the commercialized antibiotics are evaluated for their antibacterial activity and a comparison with the synthesized complexes present in this investigation was drawn.

#### 2.4. Instruments

Potentiometric measurements were made using a Metrohm 686 titroprocessor equipped with a 665 Dosimat (Switzerland-Herisau). A thermostatted glass-cell equipped with a magnetic stirring system, a Metrohm glass electrode, a thermometric probe, a microburet delivery tube and a salt bridge connected with the reference cell filled with 0.1 M KCl solution in which saturated calomel electrode was dipped are used. The titroprocessor and electrode were calibrated with standard buffer solutions prepared according to NBS specifications at 25.0  $\pm$  0.1 °C [19] and I = 0.1 mol dm<sup>-3</sup>, potassium hydrogen phthalate (pH 4.008) and a mixture of KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> (pH 6.865). The microchemical analysis of the separated solid chelates for C, H and N was performed in the microanalytical Center, Cairo University. The analyses were performed twice to check the accuracy of the analytical data. Infrared spectra were recorded on a 8001-PC FTIR Shimadzu spectrophotometer using KBr pellets. The solid reflectance spectra were measured on a schimadzu 3101 pc spectrophotometer. The molar conductance of the complexes was measured for  $1.00 \times 10^{-3} \text{ M}$  DMSO solutions at  $25 \pm 1$  °C using a systronic conductivity bridge type 305. The magnetic susceptibility measurements for the complexes were determined by the Gouy balance using Hg[Co(NCS)<sub>4</sub>] as a calibrant at room temperature.

The room temperature X-band ESR spectra were recorded utilizing ECS 106 ESR spectrometer in the presence of DPPH as a standard.

#### 2.5. Potentiometric titrations

Potentiometric titrations were carried out at constant temperature and in an inert atmosphere of nitrogen with CO<sub>2</sub>-free standardized 0.05 mol dm<sup>-3</sup> NaOH as titrant in a 50.0 ml solution at constant ionic strength 0.1 mol  $dm^{-3}$ , (adjusted with NaNO<sub>3</sub>). The proton association constant of the ligand (PHP) was determined potentiometrically by titration  $(1.0 \times 10^{-3} \text{ M})$  of the ligand solution (50 cm<sup>3</sup>). The stability constants of the binary complexes were determined using potentiometric data obtained from mixtures (50 cm<sup>3</sup>) of CuCl<sub>2</sub>·2H<sub>2</sub>O/NiCl<sub>2</sub>·6H<sub>2</sub>O (1.0  $\times$  10<sup>-3</sup> M): PHP in a concentration ratio 1:1 and 1:2 at ionic strength of (0.1 M) NaNO<sub>3</sub>. The pH meter readings were converted into hydrogen ion concentration by titrating a standard acid solution (0.05 mol  $dm^{-3}$ ), the ionic strength of which was adjusted to 0.1 mol dm<sup>-3</sup>, with standard base solution (0.05 mol dm<sup>-3</sup>) at 25 °C. The pH is plotted against p[H]. The relationship pH - p[H] = 0.05 was observed.  $[OH^{-}]$  value was calculated using a pK<sub>w</sub> value of 13.997 [20]. For the variable temperature studies the following values of  $pK_w$  were employed at 20 °C (pK<sub>w</sub> = 14.146), at 30 °C (pK<sub>w</sub> = 13.833), at 35 °C  $(pK_w = 13.680)$  and at 40 °C  $(pK_w = 13.535)$ . The ionic strength was adjusted to 0.1 mol dm<sup>-3</sup> by using NaNO<sub>3</sub>. The equilibrium constants evaluated from the titration data (summarized in Table 1) are defined by Eqs. (1) and (2), where M, L and H stand for the  $Cu^{2+}/Ni^{2+}$  ion, (PHP) and proton, respectively,

$$pM + qL + rH \rightleftharpoons M_p L_q H_r \tag{1}$$

$$\beta_{pqr} = \frac{[M_p L_q H_r]}{[M]^p [L]^q [H]^r}$$
(2)

Table 1			
Analytical data	of ligand	and their	complexes.

Compound	Yield %	M.wt.	Found% (Calcd.)	Found% (Calcd.)		
			С	Н	Ν	Cl
PHP:C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O	82%	162	66.68(66.66)	6.18(6.17)	17.26(17.28)	
THP:C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O	77%	176	68.20(68.18)	6.83(6.82)	15.92(15.91)	
CHP:C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> OCl	72%	196.5	54.99(54.96)	4.59(4.58)	14.29(14.24)	18.11(18.06)
[(PHP) <sub>2</sub> Cu]Cl <sub>2</sub> ·H <sub>2</sub> O	69%	476.5	45.35(45.33)	4.62(4.61)	11.79(11.75)	14.93(14.90)
[(THP) <sub>2</sub> Cu]Cl <sub>2</sub> ·2H <sub>2</sub> O	67%	522.5	45.94(45.93)	5.38(5.35)	10.78(10.71)	13.61(13.58)
[(CHP) <sub>2</sub> Cu]Cl <sub>2</sub> ·H <sub>2</sub> O	60%	527.5	40.97(40.94)	3.81(3.79)	10.65(10.61)	13.50(13.45)
[(PHP) <sub>2</sub> NiCl <sub>2</sub> ]·H <sub>2</sub> O	70%	471.69	45.81(45.79)	4.67(4.66)	11.90(11.87)	15.08(15.05)
[(THP) <sub>2</sub> NiCl <sub>2</sub> ] ·H <sub>2</sub> O	65%	499.69	48.04(48.03)	5.22(5.20)	11.22(11.20)	14.28(14.21)
[(CHP) <sub>2</sub> NiCl <sub>2</sub> ]	61%	522.69	41.35(41.32)	3.46(3.44)	10.74(10.71)	13.61(13.58)

Table 2

Tentative assignment of the important infrared bands of ligands and their complexes.

Compound	$v_{\rm NH}$	$v_{H_2O}$	UC=0	UC=N	$v_{M-N}$	$v_{\rm M-O}$
PHP	3251 ms, 3446 mbr		1651 s	1602 s		
THP	3249 ms, 3446 mbr		1653 s	1599 s		
CHP	3228 ms, 3444 mbr		1651 s	1600 s		
$[Cu(PHP)_2]Cl_2 \cdot H_2O$	3210	3510 mbr	1632 m	1579 m	420 w	528 w
[Cu(THP)2]Cl2·2H2O	3205	3500 mbr	1635 m	1580 m	425 w	518 w
$[Cu(CHP)_2]Cl_2 \cdot H_2O$	3190	3520 mbr	1629 m	1590 m	415 w	510 w
[Ni(PHP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	3301	3505 mbr	1620 s	1533 m	465 w	508 w
[Ni(THP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	3315	3498 mbr	1618 s	1626 m	470 w	517 w
[Ni(CHP) <sub>2</sub> Cl <sub>2</sub> ]	3305		1619 s	1520 m	468 w	510 w

Note: s, strong; w, weak; m, medium; br, broad; ms, medium strong; mbr, medium broad.

The calculations were obtained from *ca.* 100 data points in each titration using the computer program MINIQUAD-75 [21]. The stoichiometry and stability constants of the complexes formed were determined by trying various possible composition models. The model selected gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals, as described elsewhere [21]. The fitted model was tested by comparing the experimental titration data points and the theoretical curve calculated from the values of the acid dissociation constant of the ligand and the formation constants of the corresponding complexes. The results are summarized in Tables 1 and 2. The species distribution diagrams were obtained using the program SPECIES [22] under the experimental conditions employed. All measurements were carried out in our laboratory in Cairo University.

#### 3. Results and discussion

The interaction of hydrazone ligands with  $MCl_2$  [M =  $Cu^{2+}$  or  $Ni^{2+}$ ] in a molar ratio 1:2 [M:L] under reflux conditions gave the products presented in Table 1. The formulation of these complexes based on the elemental analysis, IR, EPR, UV–Vis and electrical conductivity.

#### 3.1. Conductivity measurements

The molar conductivity values for freshly prepared DMSO solutions of the complexes indicated that Cu(II) complexes are electrolytes while Ni(II) complexes are nonelectrolytes. This is in accordance with the fact that conductivity values for a nonelectrolyte are below  $50 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in DMSO solution [23,24]. The nonelectrolytic nature of the Ni(II)-complexes implies the contribution of chloride ions to the coordination sphere in the complexes under investigation. Spectral methods and elemental analysis identified complexes as [Cu(HL)<sub>2</sub>]Cl<sub>2</sub>·nH<sub>2</sub>O and [Ni(HL)<sub>2</sub>Cl<sub>2</sub>·nH<sub>2</sub>O.

#### 3.2. Infrared spectra

In absence of a powerful technique such as X-ray crystallography, IR spectra has proven to be the most suitable technique to give enough information to elucidate the way of bonding of the ligands to the metal ions. The main IR spectral bands with their tentative assignments for the free ligands and their metal (II) complexes are given in Table 2 revealing the following features.

- (1) The spectra of all ligands display sharp medium absorption band in the range 3228–3251 cm<sup>-1</sup> range and broad medium band centered at 3444–3446 cm<sup>-1</sup>. The medium band centered at 3228–3251 cm<sup>-1</sup> range is due to the different vibrational modes of –NH– of the hydrazo moiety whereas the broad band at *ca.* 3444–3446 cm<sup>-1</sup> could be taken as an evidence for the involvement of the –NH– proton in the formation of hydrogen bonding of the –NH–···O– type [25].
- (2) Hydrogen bonding may be intermolecular or intramolecular between the -NH- of the hydrazo group (Brönsted acid) and the carbonyl oxygen (Brönsted base), which means that there may be a possibility of a proton between these two groups [25]. Furthermore, the presence of proton donors and proton acceptors is prevalent in biological systems. Thus, Scheme 3, could be assumed for the ligands in the solid state.
- (3) The spectra of the free ligands display bands at 1651–1653 and 1599–1602 cm<sup>-1</sup> due to v(C=O) and v(C=N), respectively. The spectra of complexes showed that these two bands of the free ligands were not observed at the same frequencies and the same intensities. They shift to lower frequencies and, at the same time, their intensities are lowered. These results indicate that the ligands act as neutral bidentate bonded to the metal through the azomethine-nitrogen and the keto-oxygen atoms.
- (4) Further proof for the involvement of both azomethine-nitrogen and the keto-oxygen atoms in complexation is the appearance of weak bands in the far IR region of complexes



Scheme 3. Intramolecular (I) and Intermolecular hydrogen bonding (II).

at (428–470) and (508–530) cm<sup>-1</sup> due to *v*(M–N) [26] and *v*(M–O), respectively [27] which are absent in the free ligands.

- (5) The appearance of v(C=0) and the disappearance of frequency bands of the azo group in the free ligands suggest that there is no hydrazo-azo transformation; this is similar to that reported in the literature [28].
- (6) From the above-mentioned points (4) and (5), the ligands, act as neutral bidentate chelating agents coordinated to the metal via the azomethine-nitrogen and carbonyl oxygen atoms forming the more stable five membered chelate rings.
- (7) The OH stretching frequency appears in the spectra of metal complexes around 3450 cm<sup>-1</sup> is attributed to the presence of water of hydration. Also, according to Stefov et al. [29], coordinated water should exhibit frequencies at 825, 575 and 500 cm<sup>-1</sup>. The absence of spectral bands in these regions in the spectra of complexes indicates that the water molecules in these complexes are not coordinated but are present as lattice water.

#### 3.3. Magnetic and spectral data

#### 3.3.1. Ni(II) complexes

The electronic spectra of Ni(II) complexes displayed three bands at 10 050–10 116 cm<sup>-1</sup> ( $v_1$ ), 15 715–16 290 cm<sup>-1</sup> ( $v_2$ ) and 23 450– 23 580 cm<sup>-1</sup> ( $v_3$ ) (Table 3) corresponding to  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$ ,  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$  and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$  transitions, respectively, char-

#### Table 3

Molar conductance, magnetic moment and electronic spectral data of the complexes.

acteristic of octahedral geometry [30,31]. The ligand field parameter  $\Delta_0$  (splitting parameter), B' (Racah parameter of interelectronic ratio) for the nickel(II) complexes are calculated using the following equations:

$$\Delta_o = \upsilon 1 \tag{3}$$

$$B' = v_2 + v_3 - 3v_1/15 \tag{4}$$

$$\beta = B'/B^0 \tag{5}$$

where  $B^0 = 1041 \text{ cm}^{-1}$  for the free Ni<sup>2+</sup> ion. The values of  $D_0$  for the nickel(II) complexes (Table 4) are found to be in the range 1005-1012 cm<sup>-1</sup> range, indicating the intermediate ligand field position of the ligands in the nephlauxetic series. The values of transition ratio  $v_2/v_1$  and  $D_q/B'$  lies in the range 1.56–1.61 and 1.60–1.67, respectively, providing further evidence for octahedral geometry for nickel(II) complexes. The interelectronic repulsion parameter B' was calculated and found to be 601–632 cm<sup>-1</sup> for Ni(II) complexes. These values are lower than that for the free  $Ni^{2+}$  ion (1041 cm<sup>-1</sup>) which was attributed to orbital overlap and delocalization of the electrons over the molecular orbital that encompasses both the metal and the ligands. Furthermore, the values of B' showed that the  $e_g$ -electrons are  $\sigma$ -antibonding and spend some of their time on the ligand. The  $t_{2g}$ -electrons may become  $\pi$ -bonding or antibonding and spend more of their time on the ligand. Such delocalization leads to increase in the mean distance between the d-electrons and therefore increases the interelectronic repulsion parameter  $B^0$ . The nephlauxetic ratio  $\beta = B'/B^0$  for the complexes (Table 4) are less than unity suggesting the presence of electron delocalization over

Complex	$\Lambda_{M}^{a}$	M <sub>eff</sub> (B.M.)	$\lambda_{\max}$ (cm <sup>-1</sup> )			
			$n \rightarrow \pi^{*}$	$\pi \to \pi^{^*}$	d–d transition	Assignment
PHP			340	284		
THP			342	282		
CHP			341	281		
$[Cu(PHP)_2]Cl_2 \cdot H_2O$	77.2	1.68	315	235	15 625	$^{2}B_{1g} \rightarrow ^{2}B_{2g}$
[Cu(THP) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	72.2	1.72	320	237	15 723	$^{2}B_{1g} \rightarrow ^{2}B_{2g}$
$[Cu(CHP)_2]Cl_2 H_2O$	69.3	1.76	322	240	15 873	$^{2}B_{1g} \rightarrow ^{2}B_{2g}$
[Ni(PHP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	6.76	2.92	337	280	10 050	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$
					15 715	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$
					23 450	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$
[Ni(THP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	5.23	3.10	332	275	10 100	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$
					15 940	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$
					23 550	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$
[Ni(CHP) <sub>2</sub> Cl <sub>2</sub> ]	4.01	2.98	327	270	10 116	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$
					16 290	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$
					23 580	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$

<sup>a</sup> Molar conductance measured for  $10^{-3}$  M DMSO solution,  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

# Table 4Electronic spectral parameters for the octahedral nickel(II) complexes.

Complex	$\upsilon_1$	$v_2$	$\upsilon_3$	$v_2/v_1$	$D_{ m q}$	Β'	β	$D_{ m q}/{ m B}'$
$ \begin{array}{l} [Ni(PHP)_2Cl_2] \cdot H_2O \\ [Ni(THP)_2Cl_2] \cdot H_2O \\ [Ni(CHP)_2Cl_2] \end{array} $	10 050	15 715	23 450	1.56	1005	601	0.58	1.67
	10 100	15 940	23 550	1.58	1010	613	0.59	1.65
	10 116	16 240	23 590	1.61	1012	632	0.61	1.60

#### Table 5

Electron spin resonance data.

Complex	$g_{  }$	$g_{\perp}$	$g_{\rm avg}$	G
$\label{eq:cu_eq} \begin{split} & [Cu(PHP)_2]Cl_2 \cdot H_2O \\ & [Cu(THP)_2]Cl_2 \cdot 2H_2O \\ & [Cu(CHP)_2]Cl_2 \cdot H_2O \end{split}$	2.188	2.051	2.09	3.81
	2.180	2.052	2.11	3.57
	2.168	2.047	2.08	3.70

all the molecular orbitals and therefore a covalent character of nickel(II)-ligand bonds. It is well known that magnetic susceptibility measurements provide information to characterize the structure of the complexes. The room temperature magnetic moment of nickel(II) complexes lies in the range 2.92–3.10 B.M., corresponding to three unpaired electrons and in the range of an octahedral Ni(II) complexes [32,33].

# 3.3.2. Cu(II) complexes

In general, due to Jahn–Teller distortion Cu(II) complexes give absorption band between 16 667 and 14 286 cm<sup>-1</sup>. The electronic spectra of copper(II) complexes show absorption band in the range 15 625–15 873 cm<sup>-1</sup> assignable to  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$  transition of square planar geometry [30,34,35]. No absorption bands are observed below 10 000 cm<sup>-1</sup> in any complex under study which rules out the possibility of tetrahedral geometry [36,37]. Copper (II) complexes are paramagnetic and the room temperature magnetic moment values ranging from 1.68 to 1.76 B.M. are close to the spin only value of 1.70 B.M. indicate the presence of one unpaired electron and demonstrate that these complexes are monomeric in nature and the absence of metal–metal interaction.

3.3.2.1. EPR spectra. The X-band ESR spectra of the isolated copper(II) solid complexes recorded at room temperature provides information about the square planar geometry of the copper(II) complexes. The spectra are anisotropic and exhibit axial type signals with two "g" values corresponding to  $g_{\parallel}$  and  $g_{\perp}$  (Table 5). The  $g_{\parallel}$  and  $g_{\perp}$  values are computed from the spectrum using DPPH free radical as "g" marker. The ordering of g values ( $g_{\parallel} > g_{\perp} > 2.003$ )

observed for copper(II) complexes indicates that the unpaired electron is localized in  $(d_{x^2-y^2})$  orbital [38] of the Cu(II) ion (spectroscopic state <sup>2</sup>B<sub>1g</sub>) and the spectral features are characteristics of axial symmetry [39]. The values of  $g_{av}$  were calculated according to the equation  $g_{av} = 1/3[g_{||} + 2g_{\perp}]$  and the results are given in Table 5.  $g_{||}$  is a moderately sensitive function for M–L bond nature. Kivelson and Neiman [40] have reported the  $g_{||}$  value <2.3 for covalent character of metal–ligand bond and  $g_{||}$  values (Table 5) are less than 2.3 is an indication of significant covalent bonding in copper(II) complexes. Based on elemental analysis, IR, electronic spectra and ESR data, all complexes have a square planar structure.

The geometric parameter *G*, which is a measure of the exchange interaction between copper centers in the polycrystalline compound, is calculated using Hathway expression  $(G = g_{\parallel} - 2.0023)$   $g_{\perp} - 2.0023$ ) [41,42]. According to Hathway, if the value of G > 4, the exchange interaction is negligible in solid complexes but G < 4 indicates considerable interaction in solid complexes. In the complexes reported in this paper the 'G' values (3.70-3.81) < 4, indicating some weak exchange interaction between the copper(II) centers in the solid phase.

#### 3.4. Structural interpretation

From all of the above observation and according to the data reported in this paper based on the IR, molar conductivity, spectral(solid reflectance) and magnetic measurements, the structure of these complexes is given as shown in Scheme 4. The structure proposed for Cu(II)-complexes is square planar while for Ni(II)complexes is octahedral. This indicates that, the ligand behaves as bidentate chelating ligand and both azomethine nitrogen and keto oxygen are the two sites of coordination.

# 3.5. Equilibrium studies

The proton association constant corresponding to NH group of (PHP) is determined (Table 6). The PHP ligand titration curve in





#### Table 6

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Thermonynamic haramelers for the	DEVENDENTION OF ABA DOTUG IN TURBORS	$s_{0}$
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<i>T</i> (°C)	log K	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$	$\Delta S^0$
20	11.23(±0.02)	$-63.00 \pm 1.7$	$-8.45 \pm 0.6$	178.5 ± 3.4
25	10.98(±0.01)	$-62.65 \pm 1.4$		
30	10.78(±0.01)	$-62.54 \pm 1.3$		
35	10.51(±0.02)	$-61.98 \pm 1.4$		
40	10.26(±0.02)	$-61.49 \pm 1.1$		

Standard deviations are given in parentheses.

#### Table 7

Stepwise stability constants for the complexes of PHP with Cu(II) and Ni(II) metal ions in aqueous solution at I = 0.1 mol dm<sup>-3</sup> NaNO<sub>3</sub>.

T (°C)	$\log K_1(\pm\sigma)^{\mathrm{a}}$		$\log K_2(\pm\sigma)$		$\log K_1 - \log K_2$	$\log K_1 - \log K_2$	
	CuL	NiL	CuL <sub>2</sub>	NiL <sub>2</sub>	Cu(II) complex	Ni(II) complex	
20	6.99(±0.01)	5.24(±0.02)	6.41(±0.02)	4.36(±0.03)	0.58	0.88	
25	6.89(±0.02)	5.17(±0.01)	6.32(±0.01)	4.31(±0.02)	0.57	0.86	
30	6.79(±0.01)	5.10(±0.01)	6.24(±0.01)	4.25(±0.01)	0.55	0.85	
35	6.70(±0.01)	5.04(±0.01)	6.16(±0.07)	4.20(±0.01)	0.54	0.84	
40	6.63(±0.01)	4.97(±0.02)	6.08(±0.01)	4.16(±0.02)	0.55	0.81	

<sup>a</sup> ( $\sigma$ ) is the standard deviation; L = PHP.

presence and absence of metal ion (Cu<sup>2+</sup> or Ni<sup>2+</sup>) are compared. The metal–ligand titration curves lie below the curve of the ligand, which can be attributed to the liberation of proton(s) through displacement by the metal ions during complex formation. The potentiometric data of the divalent metal ions with PHP provide a good fit assuming the formation of M(PHP) (1 1 0) and M(PHP)<sub>2</sub> (1 2 0) species. Table 7 shows that (log  $K_1 - \log K_2$ ) values are usually positive, since the coordination sites of the metal ions are more freely available for binding of the first ligand than the second. The magnitude of stability constants of Cu(II) complexes with PHP is greater than those of Ni(II) complexes. The greater stability of Cu<sup>2+</sup> complexes is produced by the well-known Jahn–Teller effect.

#### 3.5.1. Species distribution curves

Estimation of equilibrium concentrations of Cu(II) and Ni(II) complexes with hydrazone ligands as a function of pH provides a useful picture of metal(II) binding in the biological system. The concentration distribution diagram of Ni(II) with (PHP) as a representative example of metal complexes is shown in Fig. 1. Ni(PHP)<sub>2</sub> complex starts to form at pH 5 in the acidic pH range and reaches a constant concentration of 97% starting from pH 9.0.

#### 3.5.2. Effect of temperature

The values obtained for  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  associated with protonation of hydrazone ligands and their complex formation with divalent Cu(II) and Ni(II) ions were calculated from the temperature dependence of the data in Tables 6 and 7. The enthalpy change ( $\Delta$ H) for the protonation of ligand or complexation process was calculated from the slope of the plot (log K versus 1/*T*) (Figs. 2–4) using Van't Hoff equation (6):

$$\log K = -(\Delta H^0/2.303R)(1/T) + \Delta S^0/R$$
(6)

From the free energy change ( $\Delta G$ ) and ( $\Delta H$ ) values one can deduce the entropy change ( $\Delta S$ ) using the well-known relationships (7) and (8):

$$\Delta G^0 = -2.303 RT \log K \tag{7}$$

 $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T \tag{8}$ 

where the gas constant  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ , *K* is the protonation constant for the ligand or the stability constant of the complex,

and *T* is the absolute temperature. The calculated thermodynamic functions are recorded in Table 8 and can be interpreted as follows:

(1) The protonation reaction of PHP can be represented by Eq. (9) as follows:

$$L^{-} + H^{+} \leftrightarrows LH. \tag{9}$$

The thermodynamic processes accompanying the protonation reaction are:

- a. The neutralization reaction, which is an exothermic process;
- b. Desolvation of ions, which is an endothermic process;
- c. The change in the configuration and the arrangements of the hydrogen bonds around the free and protonated ligands.
- (2) The log *K*<sup>H</sup> value decrease with increasing temperature revealing that its acidity increases with increasing temperature [43].
- (3) A negative value of  $\Delta H^0$  for the protonation process of PHP ligand indicates that its association process is accompanied by a release of heat and the process is exothermic.
- (4) The protonation reaction of hydrazone ligand has positive entropy; this may be due to increased disorder as a result of desolvation processes and the breaking of hydrogen bonds.

The stepwise stability constants of the complexes formed at different temperatures were calculated and the average values are included in Table 8. Examination of these values reveals that:

- 1. The stepwise stability constants  $(\log K_1 \text{ and } \log K_2)$  for the complexes decrease with increasing temperature, i.e. their stabilities decrease with increasing temperature and complexation process is more favorable at lower temperatures [44].
- 2. All values of  $\Delta G^0$  for complexation are negative, indicating the spontaneity of the coordination process.
- 3. The negative values of  $\Delta H^0$  show that the coordination process is exothermic, indicating that the complexation reactions are favored at low temperatures.
- 4. It is generally noted that  $\Delta G^0$  and  $\Delta H^0$  values for the 1:1 complexes are more negative than those corresponding to the 1:2 complexes, Table 8. This may be attributed to the steric hindrance produced by the entrance of a second ligand.



**Fig. 1.** Concentration distributions of various species as a function of pH of Ni(II)–PHP system at concentration of  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, for Ni(II) and  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> for PHP, I = 0.1 mol dm<sup>-3</sup> at 25 °C.



Fig. 2. Van't Hoff plot of log K<sub>protonation</sub> of PHP ligand.

5. The  $\Delta S^0$  values for all investigated complexes are positive, indicating that the increase in entropy by the release of bound solvent molecules on coordination is greater than the decrease resulting from the coordination process itself. It occurs because the solvent molecules arranged in an orderly fashion around the ligand and the metal ion has acquired a more random configuration on coordination [44].

# 3.6. Antimicrobial activity

The question about the involvement of the metal complexes in medical treatment is of special interest. To assess the biological potential of the synthesized compounds, the hydrazone ligands and their metal complexes were tested against different species of bacteria and fungi. In testing the antimicrobial activity of these compounds, we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The results of the antimicrobial activity of the synthesized compounds are recorded in Table 9. The data obtained reflect the following results:

1. The synthesized complexes were found to be more toxic compared with their parent free ligands against the same microorganism and under the identical experimental conditions. The increase in biological activity of the metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of toxicity increase may be considered in the light of Tweedy's chelation theory [45]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor group and possible  $\pi$ -electron delocalization within the whole chelate ring system that is



**Fig. 3.** Van't Hoff plot of  $\log K_1$  of Cu(II) and Ni(II) complexes with PHP.



Fig. 4. Van't Hoff plot of log K<sub>2</sub> of Cu(II) and Ni(II) complexes with PHP.

Table 8
Thermodynamic parameters <sup>a</sup> for Cu(II) and Ni(II) complexes of PHP in aqueous solution at $I = 0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ .

<i>T</i> (°C)	$-\Delta G_1^0$ (k]	mol <sup>-1</sup> )	$-\Delta G_2^0$ (kJ	$mol^{-1})$	$-\Delta H_1^0$ (kJ	$mol^{-1})$	$-\Delta H_2^0$ (k]	$mol^{-1}$ )	$\Delta S_1^0$ (J K	$^{-1}$ mol $^{-1}$ )	$\Delta S_2^0$ (J K <sup>-1</sup>	$^{1}  mol^{-1})$
	CuL	NiL	CuL <sub>2</sub>	NiL <sub>2</sub>	CuL	NiL	CuL <sub>2</sub>	NiL <sub>2</sub>	CuL	NiL	CuL <sub>2</sub>	NiL <sub>2</sub>
20	39.21	29.39	35.96	24.46	32.67	23.89	28.80	17.92	22.2	18.8	24.4	22.2
25	39.31	29.50	36.06	24.59								
30	39.39	29.58	36.20	24.67								
35	39.51	29.72	36.33	24.77								
40	39.67	29.79	36.44	24.93								

 $^{a} \text{ Standard deviations, } -\Delta G_{1}^{0} \pm (0.29 - 0.85); -\Delta G_{2}^{0} \pm (0.51 - 0.95); -\Delta H_{1}^{0} \pm (0.49 - 0.93); \\ \Delta H_{2}^{0} \pm (0.78 - 1.12); \\ \Delta S_{1}^{0} \pm (0.99 - 1.43); \\ \Delta S_{2}^{0} \pm (0.83 - 1.28); \\ L = PHP. \\ \Delta S_{1}^{0} \pm (0.29 - 0.85); -\Delta S_{2}^{0} \pm (0.51 - 0.95); \\ \Delta S_{2}^{0} \pm (0.29 - 0.85); \\ \Delta S_{2}^{0} \pm (0.29$ 

formed during coordination. Such chelation could enhance the lipophilic character of the central metal atom and hence increase the hydrophobic character and liposolubility of the complex favoring its permeation through the lipid layers of the cell membrane. This enhances the rate of uptake/entrance and thus the antimicrobial activity of the testing compounds.

#### Table 9

Antimicrobial activity of the free ligands and isolated complexes.

Compound	Gram-positive	Gram-negative		Fungi	Fungi		
	Staphylococcus aureus	Pseudomonas aereuguinosa	Escherichia coli	Candida albican	Candida lypolytic		
PHP	_	_	_	+	+		
THP	_	_	-	+	+		
CHP	_	_	-	+	+		
[Cu(PHP)2]Cl2·H2O	++++	++	++	+++	+++		
[Cu(THP)2]Cl2·2H2O	++	++	++	++	++		
[Cu(CHP) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	+++	++	++	+++	++		
[Ni(PHP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	++	+	+	++	+++		
[Ni(THP) <sub>2</sub> Cl <sub>2</sub> ]·H <sub>2</sub> O	+	+	+	+	+		
[Ni(CHP) <sub>2</sub> Cl <sub>2</sub> ]	+	+	+	++	++		
Amikacin	R	+++					
Augmantin	+++	R					
Septrin	R	R					
Cefobid	R	R					
Erythromycin	+++	R					
Ampicillin	R	+ +					

Note: (1) The test was done using the disc diffusion method.

(2) (-) = non-detected (resistance).

(3) Zone of inhibition as ++++ = (20–25 mm) (very active).

(4) Zone of inhibition as +++ = (15–20 mm) (highly active).

(5) Zone of inhibition as ++ = (10-15 mm) (moderately active).

(6) Zone of inhibition as + = (5-10 mm) (moderately active).

Accordingly, the antimicrobial activity of the complexes present in this investigation can be referred to the increase of their lipophilic character which in turn deactivates enzymes responsible for respiration processes and probably other cellular enzymes, which play a vital role in various metabolic pathways of the tested micro-organisms.

- 2. Antibacterial activity of all complexes towards *Escherichia coli* are detected.
- 3. Structure–activity relationships evidence that the complexation with copper enhances the antimicrobial activity of the ligands against some of the tested organism. Since copper chelates have an enhanced antimicrobial activity, in comparison to their analogous containing nickel(II) ion, the metal seems to play a relevant role in the activity of these compounds. A similar behavior of the increased antibacterial activity was also exhibited by copper derivatives of 2,6-diacetylpyridine bis(2-thenoylhydrazone) in comparison to the corresponding Co(II), Ni(II) and Zn(II) chelates [46].
- 4. The tested complexes were more active against Gram-positive than Gram-negative bacteria, it may be concluded that the antimicrobial activity of the compounds is related to cell wall structure of the bacteria. It is possible because the cell wall is essential to the survival of bacteria and some antibiotics are able to kill bacteria by inhibiting a step in the synthesis of peptidoglycan. Gram-positive bacteria possess a thick cell wall containing many layers of peptidoglycan and teichoic acids, but in contrast, Gram-negative bacteria have a relatively thin cell wall consisting of a few layers of peptidoglycan surrounded by a second lipid membrane containing lipopolysaccharides and lipoproteins. These differences in cell wall structure can produce differences in antibacterial susceptibility and some antibiotics can kill only Gram-positive bacteria and is infective against Gram-negative pathogens [47].
- The free ligands and their synthesized complexes were found to have antifungal activity toward *C. albican* and *C. lypolytic* fungi.
- 6. Furthermore, some known antibiotics are tested toward S. aureus (as Gram-positive) and P. aereuguinosa (as Gram negative). The selected antibiotics are Amikacin, Augmantin, Septrin, Cefobid, Ampicillin and Erythromycin. The given data in Table 9 show that Amikacin, Septrin, Cefobid, and Ampicillin antibiotics have resistance effect toward S. aureus in contrast to the synthesized

complexes. In the same connection, *Augmantin*, *Septrin*, *Cefobid* and *Erythromycin* have resistance effect toward *P. aereuguinosa* while all synthesized complexes have a greater effect.

7. Cu(II) complexes have a greater or comparable effect than the effect of all tabled antibiotics against Gram-positive bacteria.

# 4. Conclusions

The present paper reports on the synthesis, characterization and their electronic absorption spectra of hydrazone ligands and their Cu(II) and Ni(II) complexes. The synthetic procedure in this work resulted in the formation of complexes in the molar ratio (1:2) (M:L), respectively. In these complexes the hydrazone ligand acts as a neutral bidentate ligand and coordinated to metal ion through the azomethine-nitrogen and keto-oxygen atoms forming stable five membered heterocyclic rings. The present study revealed octahedral geometry around Ni(II)-complexes and square planar geometry around Cu(II)-complexes. From conductance measurements Cu(II)-complexes are electrolytes while Ni(II)-complexes are non-electrolytes. The ionization constant of the investigated ligand (PHP) has been determined potentiometrically. Also, the present investigation described the formation equilibria of Cu(II) or Ni(II) with PHP and from the above-mentioned results it may be concluded that:

- (a) The formation of the metal complexes has been found to be spontaneous, exothermic and entropically favorable.
- (b) The values of  $\log K_1 \log K_2$  are positive, indicating that the coordination of the first ligand molecule (PHP) to the metal ion is more favorable than the bonding to the second one.

The results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to the parent ligand under identical experimental conditions. The antibacterial activity has been explained on the basis of chelation theory. Also, the results indicated that tested complexes were more active against Gram-positive than Gram-negative bacteria. It may be concluded that antibacterial activity of the compounds is related to cell wall structure of the bacteria. It is possible because the cell wall is essential to the survival of many bacteria and some antibiotics are able to kill bacteria by inhibiting a step in the synthesis of peptidoglycan.

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